

Direct evidence of rigidity loss and self-organisation in silicate glasses

Y. Vaills¹, T. Qu², M. Micoulaut³, F. Chaimbault¹ and P. Boolchand²

¹ *Universit d'Orlans 45067 Orlans Cedex 02 and
Centre de Recherches sur les Matériaux Haute Température, 1D avenue de la recherche scientifique,
45071 Orlans Cedex 02, France*

² *Department of Electrical and Computer Engineering and Computer Science, University of
Cincinnati, OH 45221-0030*

³ *Laboratoire de Physique Thorique des Liquides, Universit Pierre et Marie Curie, Boite 121
4, Place Jussieu, 75252 Paris Cedex 05, France*

(February 2, 2008)

The Brillouin elastic free energy change $\Delta\Phi$ between thermally annealed and quenched $(Na_2O)_x(SiO_2)_{1-x}$ glasses is found to decrease linearly at $x > 0.23$ (floppy phase), and to nearly vanish at $x < 0.18$ (stressed-rigid phase). The observed $\Delta\Phi(x)$ variation closely parallels the mean-field floppy mode fraction $f(x)$ in random networks, and fixes the two (floppy, stressed-rigid) elastic phases. In calorimetric measurements, the non-reversing enthalpy near T_g is found to be large at $x < 0.18$ and at $x > 0.23$, but to nearly vanish in the $0.18 < x < 0.23$ range, suggesting existence of an intermediate phase between the floppy and stressed-rigid phases.

Pacs: 61.43Fs, 63.50.+x

Silicate melts and glasses are important geophysical [1], optoelectronic [2] and microelectronic materials [3], and find applications as window glass materials, optical fibers and thin-film gate dielectrics [3]. Functionality of materials often derives from their structures at different length scales. At a basic level, the molecular structure of sodium silicate $(Na_2O)_x(SiO_2)_{1-x}$ glasses consist of a network of $Si(O_{1/2})_4$ tetrahedra in which addition of sodium oxide produces $Si(O_{1/2})_{4-m}O_mNa_m$ (or Q^{4-m} in NMR notation) local units having $m = 0, 1, 2$ and 3 non-bridging oxygen (NBO) sites attached to Na^+ ions. Addition of a few (10) mole percent of Na_2O lowers [4] the glass transition temperature, T_g , of the base (SiO_2) material ($1200^\circ C$) sharply (to $600^\circ C$) because of a loss in global connectivity as some Q^3 units ($m = 1$) emerge [5] at the expense of Q^4 ($m = 0$) ones. The sharp reduction of T_g destroys the mechanical equilibrium that prevailed [5,6] in the pristine glass ($x = 0$), and drives alloyed glasses to become stressed rigid. This is largely the case because the bond-bending constraint of bridging oxygen atoms that were intrinsically broken [6,7] at $1200^\circ C$, becomes restored in the weakly alloyed glass as T_g s plummet to $600^\circ C$. However, upon continued addition of Na_2O the alloyed glass softens as network connectedness decreases, and one expects an elastic phase transition from a stressed rigid to a floppy phase.

One can estimate the elastic phase boundary within a mean-field theory by counting the Lagrangian constraints [8,9] per atom (n_c) due to bond-stretching and bond-bending forces. The floppy mode fraction, $f(x) = (3 - n_c)/3$ extrapolates linearly [8,9] to zero as n_c increases to 3 defining the phase boundary. Physically, $f(x)$ represents the count of zero-frequency (floppy mode) solutions of the dynamical matrix in studying normal modes of a network. In the present oxide glasses, we will show latter that the condition $n_c = 3$ is met [7] when $x = 1/5$, and glass compositions at $x > 1/5$ are viewed as floppy while those at $x < 1/5$ stressed rigid. In the stressed-rigid phase, numerical simulations [10,11] on random networks using a Kirkwood-Keating potential have shown that both longitudinal (C_{11}) and shear (C_{44}) elastic constants display a power-law variation as a function of \bar{r} (mean coordination number) or x , i.e., C_{11} or $C_{44} \simeq (\bar{r} - \bar{r}_c)^p$ with $p = 1.5(1)$ with a pronounced accuracy at higher \bar{r} . Such a power-law has been observed in Raman optical elasticities [12,13] but not in bulk elasticity [14–16] measurements.

We have now examined the rigidity onset in $(Na_2O)_x(SiO_2)_{1-x}$ glasses using Brillouin scattering (BS) and Temperature Modulated Differential Scanning Calorimetry (MDSC). In this Letter, we show that the optical method [15] reveals the mean-field behavior of the elastic phase transition: the elastic energy change $\Delta\Phi(x)$ upon thermal annealing of the as quenched (virgin) glasses is lowered linearly at $x > x_c(2) = 0.238$, but to nearly vanish ($\simeq 0$) at $x < x_c(1) = 0.18$. The observed variation in $\Delta\Phi(x)$ closely parallels the floppy mode fraction $f(x)$ in random networks [10], and serves to uniquely fix glasses at $x > 0.238$ to be floppy while those at $x < 0.18$ to be stressed rigid. The stressed-rigid nature of the glasses at $x < 0.18$ is confirmed in Brillouin longitudinal ($C_{11}(x)$) and shear

($C_{44}(x)$) elastic constants that show a power-law variation with a power p of 1.68(8) and 1.69(8) in remarkable agreement with numerical simulations [10,11]. The non-mean-field behavior of the underlying rigidity transition is, however, manifested in MDSC that probes glasses at all length scales. In these calorimetric measurements, the non-reversing enthalpy (ΔH_{nr}) at the glass transition (T_g) is found to be large at $x > x_c(2) = 0.238$ and at $x < x_c(1) = 0.18$, but to nearly vanish in the $x_c(1) < x < x_c(2)$ range. The latter range, the thermally reversing window [17], is identified with intermediate phases. Thus, the use of two complimentary probes, a mean-field (optical) and a non-mean-field (calorimetric) one, has provided a rather comprehensive view of the three elastic phases, floppy, intermediate and stressed-rigid populated in an oxide glass system.

18 gram (Na_2O) $_x$ (SiO_2) $_{1-x}$ glasses over the soda concentration range $0.05 < x < 0.30$, were synthesized by reacting the starting materials in a Pt-Rh crucible heated electrically to $1500^\circ C - 1650^\circ C$ for up to 4 hours. Details of the facility are described elsewhere [18]. Melts were poured on stainless plates. Glass sample cubes 8 mm across were prepared by cutting the ingots with a diamond saw and polishing the surfaces to an optical finish. Brillouin scattering was excited with $\lambda = 514.5$ nm radiation and recorded in a right angle geometry using a pressure scanned [18], triple-pass plane Fabry-Perot interferometer with an effective finesse of 70. Spectra were recorded for virgin- and annealed-glasses. The latter samples were obtained by heating virgin glasses at $515^\circ C$ for 4 hours. Because of the hygroscopic nature of samples, the glasses were handled in a controlled environment using glove boxes. MDSC measurements were performed [13,17] using a model 2920 unit from TA Instruments Inc., at a scan rate of $3^\circ C/min$ and a modulation rate of $1^\circ C/100s$ using Au pans. MDSC measurements were undertaken on both virgin and vacuum annealed ($80^\circ C$ for 48 hours) glasses.

Brillouin lineshapes observed in the glasses (Fig. 1) show the Longitudinal Acoustic (LA) mode frequency, $\nu_{LA}(x)$, to shift to a lower frequency as x increases from 0.137 to 0.20, and then to a higher frequency at $x = 0.32$. Furthermore, mode frequency shifts due to annealing (broken-line curves) are small at low x (0.137) but pronounced at high x (0.32). The longitudinal (C_{11}) and shear (C_{44}) elastic constants were obtained using the relation, $C_{11} = \rho \nu_{LA}^2 \lambda^2 / 2n^2$ and $C_{44} = \rho \nu_{TA}^2 \lambda^2 / 2n^2$ where ν_{LA} , ν_{TA} , n and ρ represent the LA- and TA- mode frequencies, refractive index and mass density respectively. The refractive index was measured using a differential path refractometer and mass densities of virgin and annealed glasses by buoyancy method. Note that density change is here achieved by chemical alloying which influences the Brillouin lineshapes, in contrast with density changes induced by pressure or temperature [19].

Compositional trends in $C_{11}(x)$ and $C_{44}(x)$ appear in Fig. 2, and show C_{11} to decrease with x at first, and then to increase at $x > 0.20$, due to layered-like disilicate units [20] (adamantine) emerging as x increases to 1/3. On the other hand, the shear elastic constant

C_{44} systematically decreases as x increases to $1/3$. We have also obtained the elastic energy change, $\Delta\Phi(x)$, upon thermal annealing glasses using [18]:

$$\Delta\Phi = \frac{1}{6} \left(\frac{\Delta\rho}{\rho} \right) (3C_{11} - 4C_{44}) \quad (0.1)$$

and find $\Delta\Phi$ to increase linearly at $x > 0.238$, and to vanish at $x < 0.18$ as shown in Fig.2b. The free energy of the thermally relaxed glass is lowered by an amount $\Delta\Phi$ in relation to the virgin glass. Calorimetric results on the glasses using MDSC appear in Fig.3, with (a) displaying variations in $T_g(x)$ deduced from the reversing enthalpy (b) variations in the non-reversing enthalpy, $\Delta H_{nr}(x)$. We find ΔH_{nr} term is large at $x > 0.238$ and at $x < 0.18$, but the term almost vanishes (0) in the $0.18 < x < 0.23$ range particularly in the annealed glasses.

Our interpretation of the BS results is as follows. Vibrational analysis of random networks within a mean-field theory reveals the floppy mode fraction as a function of \bar{r} to be given [10] by: $f(\bar{r}) = 6 - 5\bar{r}/2$. In the present glasses, since $\bar{r} = (8 - 4x)/3$ (ref. [21]), the latter equation can be written as: $f(x) = \frac{10}{3}x - \frac{2}{3}$ which reveals $f(x)$ to increase linearly at $x > 1/5$ in the floppy phase, and $f(x) \simeq 0$ at $x < 1/5$ in the stressed-rigid phase, thus, showing the mean-field elastic phase boundary at $x_{mf} = 1/5$. More accurate numerical simulations based on a bond-depleted amorphous Si network performed by M.F.Thorpe [10] have localized the phase boundary by plotting the second derivative of $f(\bar{r})$, which shows a cusp at $\bar{r} = 2.385$. For the case of the present oxides, the corresponding phase boundary would be at [21] $x_{num} = 0.211$. The observed variation in $\Delta\Phi(x)$ (Fig.2b) mimics the results of these numerical simulations of $f(x)$, and $d^2\Delta\Phi(x)/dx^2$ shows a cusp near $x = 0.238$. Quenched glasses at $x > 0.238$ relax [18] as frozen stress is thermally annealed away by floppy or bond-rotational modes. These modes are associated with the underconstrained Q^2 and Q^1 units that grow [5] precipitously at $x > 0.25$. These modes are nearly absent in the more connected glasses ($x < 0.18$). Furthermore, since our glasses were relaxed at a fixed annealing temperature of $515^\circ C$, $\Delta\Phi(x)$ provides a measure of elastic free energy in much the same fashion that $f(x)$ is viewed [10] as the network free energy. The correlation serves to uniquely fix glasses at $x > 0.238$ to be floppy while those at $x < 0.18$ to be stressed-rigid. Here we must recall that the length scale over which BS probes the elastic behavior of glasses is set by the wavelength of the acoustic phonons that lie in $\lambda \simeq 300 \text{ nm}$ range [23]. One, therefore, expects BS to probe the average elastic behavior of the rigidity transition in the present oxide glasses as in chalcogenide glasses [15].

The calorimetric probe (MDSC) registers enthalpic changes near T_g in a glass network, and these contributions come from molecular rearrangements taking place at all length scales. And for that reason, one expects to observe non-mean-field effects associated with the elastic phase transition using the thermal probe. The existence of a thermally reversing window (Fig. 3b) is an example of such an effect [17]. We find the window sharpens and deepens upon

low-temperature thermal anneal because network stress frozen upon a quench is relieved. The window in the present oxide glasses is reminiscent of parallel results in chalcogenide glasses [12,13,17]. The observation of a reversibility window in the present oxides leads naturally to the suggestion that glasses in the $0.18 < x < 0.238$ composition range are in the intermediate phase, i.e., they are self-organized. In this range of composition, Si^{29} NMR shows [5] concentration of undersconstrained [21] Q^3 ($n_c = 2.67$) and overconstrained Q^4 ($n_c = 3.67$) units to be comparable. Self-organization effects stem [22] from the fact such a mix leads to an isostatically rigid global structure ($\bar{n}_c \simeq 3$).

The stressed rigid nature of glasses at $x < 0.18$ is confirmed by the power-law variation in $C_{11}(x)$ and $C_{44}(x)$. The variation is inferred by plotting $\log(C_{11}(x) - C_{11}(x_c(1)))$ against $\log(x_c(1) - x)$, using $x_c(1) = 0.18$, and yields (Fig. 4) $p = p_{11} = 1.68(8)$. Parallel analysis of $C_{44}(x)$ yields a power-law $p = p_{44} = 1.69(8)$. These results are in remarkable agreement with numerical predictions [10,11] of $p = 1.5(1)$ in random networks as noted earlier in Raman scattering on chalcogenide glasses [12,13]. To the best of our knowledge this is the first time one has observed a power-law variation in elastic constants for stressed rigid glasses using a bulk probe. In BS results on chalcogenide glasses [15] as in ultrasonic elastic moduli results [14,16] one could discern only a linear variation in $C_{11}(x)$. Why is the rigidity transition washed out in chalcogenide- but not in the present oxide glasses? Residual interactions due to dihedral angle forces and lone-pair van der Waals forces dilute the effect of first-neighbor (bond-stretching) and second-neighbor (bond-bending) forces and wash out the phase transition. We note that the $Si - O$ single bond strength [24] (100 kcal/mole) far exceeds the $Ge - Se$ single bond strength (40 kcal/mole). Furthermore, lone pair interactions are likely to be much weaker in the oxides than in chalcogenide glasses. It appears that the power-law variation in elastic constants is observed in those instances where first- and second-neighbor forces overwhelm residual interactions as is the case of Brillouin scattering in the oxides, or that of Raman scattering in chalcogenide [12,13].

In summary, Brillouin scattering and MDSC have permitted identifying the three elastic phases in $(Na_2O)_x(SiO_2)_{1-x}$ glasses; glasses at $x < 0.18$ are stressed-rigid, those in $0.18 < x < 0.23$ are intermediate, while those at $x > 0.23$ are floppy. A power-law variation of the longitudinal- and shear- elastic constants is observed in the stressed-rigid phase of the oxide glasses using a bulk probe (BS) for the first time. These novel results show that the floppy to stressed-rigid phase transitions in oxide and chalcogenide glasses are remarkably similar, underscoring the basic physics driving formation of elastic phases in disordered systems. Our results correlate well with electrical transport that show activation energy for diffusion [26] in the floppy glasses to be consistently low, and to increase monotonically as the backbone becomes increasingly stressed-rigid. This work is supported by a joint CNRS-NSF collaboration research project 13049 and NSF grant Int- 01-38707 and DMR-01-01808. .

-
- [1] *Structure , dynamics and properties of silicate melts*, Ed. J.Stebbins, P.McMillan, D.Dingwell, Rev. Mineral **32** (Mineral Society of America, Washington, D.C. 1995).
 - [2] S. Suzuki and Y. Abe, J.Non-Cryst. Solids **43**, 141(1981).
 - [3] G.Lucovsky, H.Y. Yang, Y Wu, H. Niimi, Thin solid films **374**, 217(2000).
 - [4] M. Micoulaut, Eur. Phys. J.B1, 277 (1998)
 - [5] H. Maekawa, T.Maekawa, K. Kawamura and T.Yokokawa, J.Non-Crystalline Solids **127**,53 (1991).
 - [6] R.Kerner and J.C. Phillips, Solid State Commun. **117**, 47 (2000).
 - [7] M.Zhang and P. Boolchand, Science **266**, 1355 (1994).
 - [8] M.F. Thorpe J.Non Cryst. Solids **34**, 153 (1979).
 - [9] J.C. Phillips J.Non Cryst. Solids **57**, 355 (1983).
 - [10] H. He and M.F. Thorpe, Phys. Rev. Lett. **54**, 2107(1985). M.F.Thorpe, D.J.Jacobs , M.V.Chubynsky and J.C.Phillips , J.Non-Cryst. Solids **266-269**, 859 (2000).
 - [11] D.S. Franzblau and J. Tersoff, Phys. Rev. Lett. **68**, 2172(1992).
 - [12] P. Boolchand, X.Feng, and W.J. Bresser, J. Non-Cryst. Solids **299**, 958 (2002).
 - [13] D. Selvanathan,W.J.Bresser, and P. Boolchand, Phys. Rev. B **61**, 15061(2000).
 - [14] J.Y.Duquesne and J.Bellesa , J.Phys.(Paris), Colloq. **46**, C10-445(1985).
 - [15] J. Gump, I Finkler, H.Xia, R. Sooryakumar, W.J.Bresser, P. Boolchand, Phys. Rev. Lett. **92**, 245501 (2004).
 - [16] S.S. Yun, Hui Li, R.L. Cappelletti, R.N. Enzweiler and P. Boolchand, Phys. Rev. B **39**, 8702 (1989)
 - [17] P. Boolchand, D.G.Georgiev, B. Goodman, J. Optoelectronics and Adv. Mater. **3**, 703(2001).
 - [18] Y. Vailis, Y. Luspín and G. Hauret, J. Non-Cryst. Solids **286**, 224 (2001).
 - [19] A. Polian, M. Grimsditch and D. Vo-Tranh, Phase Trans. **63**, 187 (1997).
 - [20] J.Olivier Fourcade, E.Phillippot, M.Ribes and M.Maurin, Rev. Chem. Miner.**9**, 757 (1972).

- [21] In $(Na_2O)_x(SiO_2)_{1-x}$ glasses, taking the coordination number of Si, Na and O to be respectively 4, 1 and 2, we obtain $\bar{r} = [4x + 8(1 - x)]/3 = (8 - 4x)/3$; For a $\bar{r} = 2.385$, the implied threshold in $x_{num} = (8 - 3\bar{r})/4 = 0.211$ for the present oxides; For $Q^4 [Si(O_{1/2})_4]$ units, the Lagrangian constraints/ atom, $n_c = (1/3)[7 + 2\frac{1}{2}4] = 3.67$; For $Q^3 [Si(O_{1/2})_3O^-Na^+]$ units, $n_c = (1/4.5)[7 + 3\frac{1}{2}2 + 1 + 1] = 2.67$.
- [22] M.Micoulaut and J.C. Phillips, Phys. Rev. B **67**, 104204 (2003).
- [23] R. Vacher, J. Pelous and E. Courtens, Phys. Rev. B **56**, R481 (1997).
- [24] L. Pauling, Nature of the Chemical Bond (Cornell University Press, 1960) p.85.
- [25] O.V. Mazurin, M.V. Strel'sina, T.P. Shvaiko -Shvaikovska, Ternary Silicate Glasses, (Elsevier, New York, 1987).
- [26] G.N. Greaves and K.L. Ngai, Phys. Rev. B **52**, 6358 (1995).

List of Figures

1	Brillouin lineshapes showing the longitudinal acoustic mode at indicated $(Na_2O)_x(SiO_2)_{1-x}$ glass compositions x . The mode shift between virgin (continuous line) and annealed (broken line) glasses is small at low x (0.137) and large at high x (0.32).	9
2	(a) Variations in $C_{11}(x)$ and $C_{44}(x)$ and (b) in elastic energy increase $\Delta\Phi(x)$ in $(Na_2O)_x(SiO_2)_{1-x}$ glasses deduced from Brillouin scattering. The continuous line and broken line give the floppy mode fraction $f(x)$ prediction for random- and self organized networks respectively. The second derivative of $\Delta\Phi(x)$ obtained from the BS results fix the mean-field elastic phase transition at $x = 0.238$, with glasses at $x > 0.238$ floppy.	10
3	MDSC results on $(Na_2O)_x(SiO_2)_{1-x}$ glasses showing variations in (a) $T_g(x)$, (b) non-reversing enthalpy $\Delta H_{nr}(x)$ for virgin (\circ) and annealed (\bullet) samples. The DSC results were taken from ref. 26.	11
4	A log log plot of $C_{11}(x) - C_{11}(0.18)$ against $(x - 0.18)$ showing a power-law variation with a power $p = 1.69(8)$ in the stressed-rigid region ($0 < x < 0.18 = x_c(1)$). Corresponding results for $C_{44}(x)$ show a power-law of 1.68(8). See text for details.	12

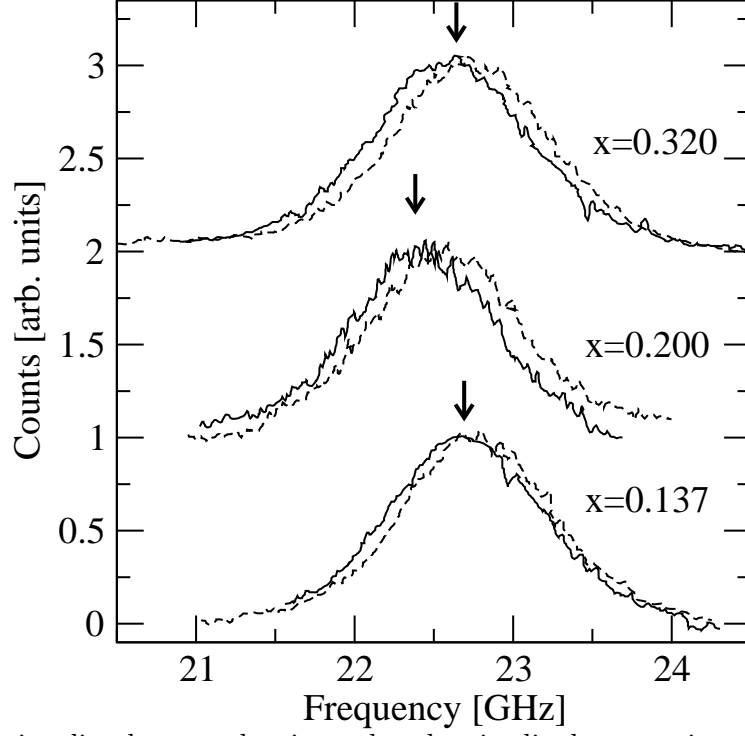


FIG. 1. Brillouin lineshapes showing the longitudinal acoustic mode at indicated $(Na_2O)_x(SiO_2)_{1-x}$ glass compositions x . The mode shift between virgin (continuous line) and annealed (broken line) glasses is small at low x (0.137) and large at high x (0.32).

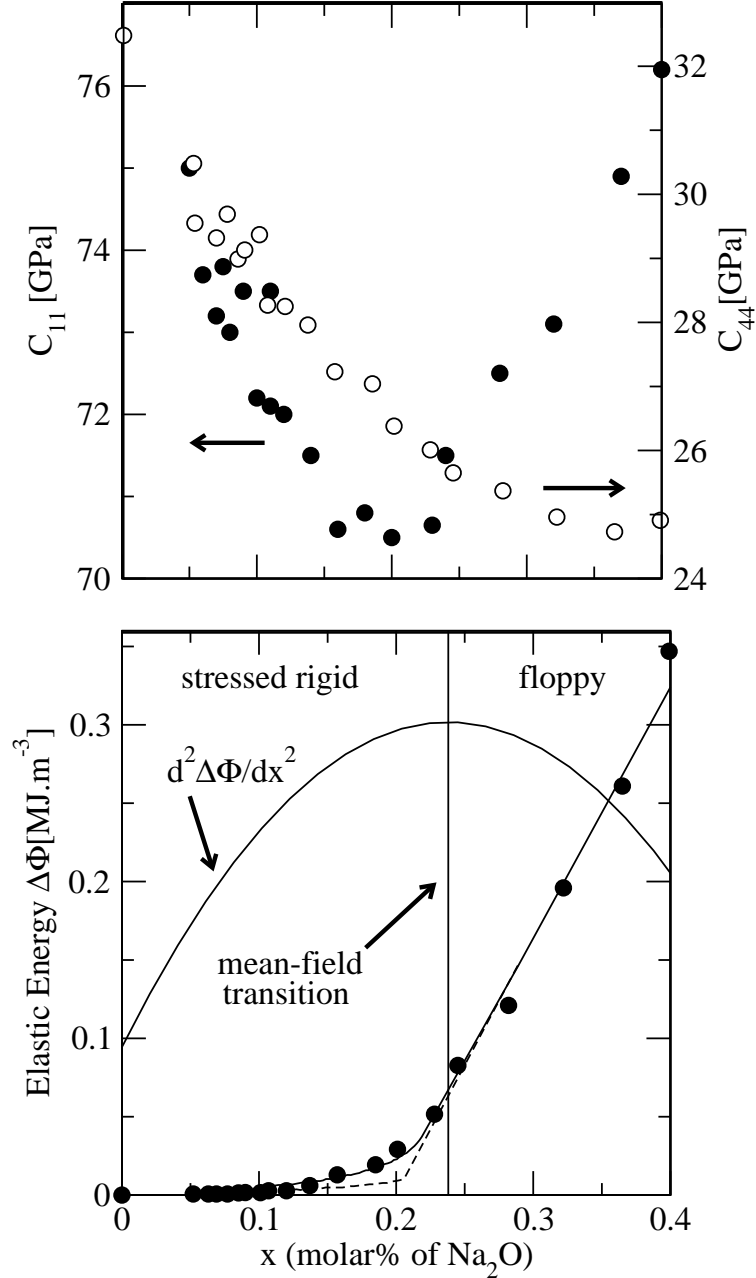


FIG. 2. (a) Variations in $C_{11}(x)$ and $C_{44}(x)$ and (b) in elastic energy increase $\Delta\Phi(x)$ in $(\text{Na}_2\text{O})_x(\text{SiO}_2)_{1-x}$ glasses deduced from Brillouin scattering. The continuous line and broken line give the floppy mode fraction $f(x)$ prediction for random- and self organized networks respectively. The second derivative of $\Delta\Phi(x)$ obtained from the BS results fix the mean-field elastic phase transition at $x = 0.238$, with glasses at $x > 0.238$ floppy.

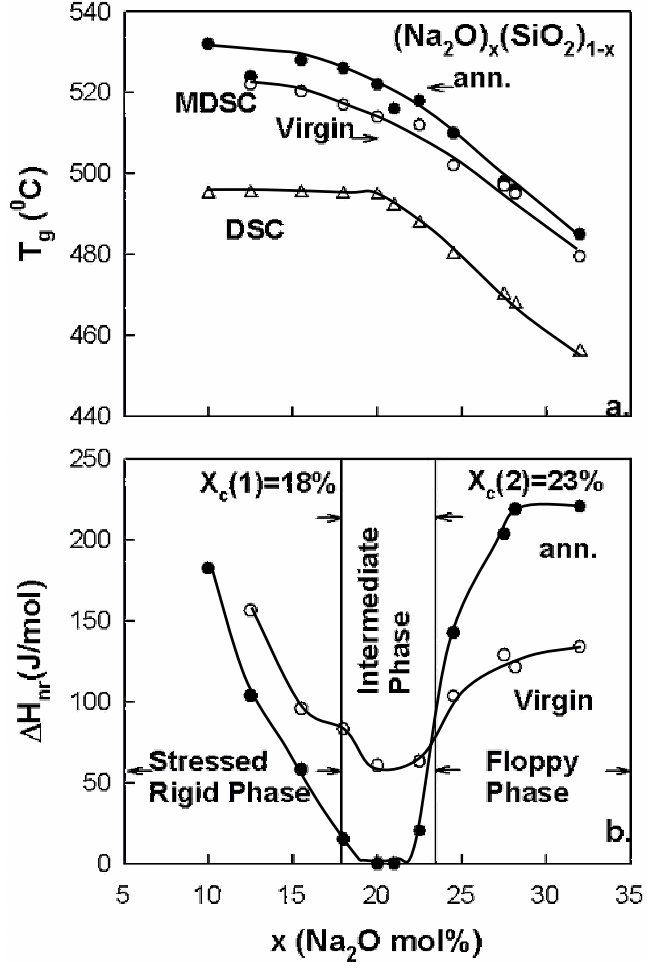


FIG. 3. MDSC results on $(\text{Na}_2\text{O})_x(\text{SiO}_2)_{1-x}$ glasses showing variations in (a) $T_g(x)$, (b) non-reversing enthalpy $\Delta H_{nr}(x)$ for virgin (○) and annealed (●) samples. The DSC results were taken from ref. 26.

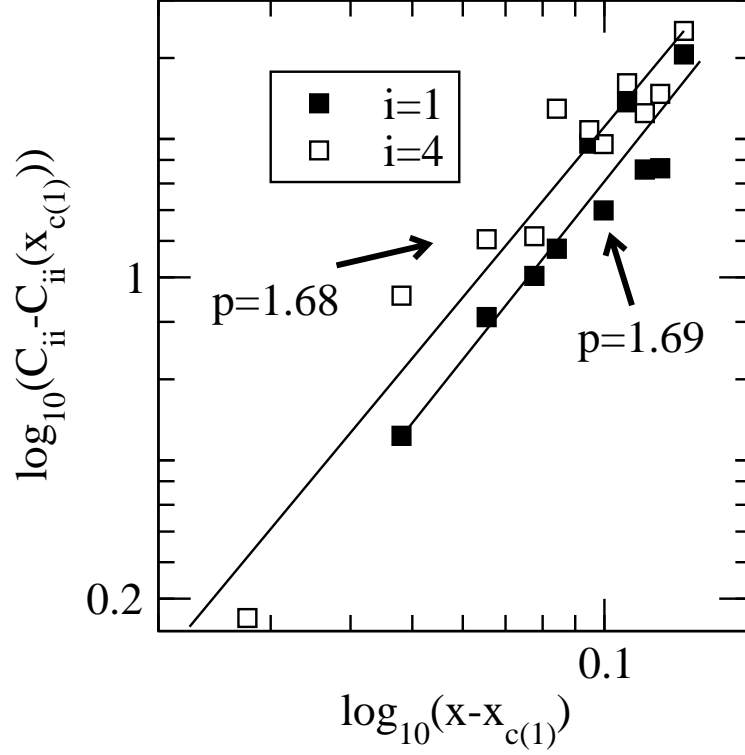


FIG. 4. A log log plot of $C_{11}(x) - C_{11}(0.18)$ against $(x - 0.18)$ showing a power-law variation with a power $p = 1.69(8)$ in the stressed-rigid region ($0 < x < 0.18 = x_c(1)$). Corresponding results for $C_{44}(x)$ show a power-law of $1.68(8)$. See text for details.